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D-14129 Berlin (DE)(54) **Method for rendering waste substances harmless.**

(57) A method is provided for the treatment of hydrocarbon-contaminated soil by chemical hydrolysis and/or oxidation of the hydrocarbons in the hydrocarbon-contaminated soil. The method includes conditioning lime with a hydrophobizing agent, the essential component of which is a mixture of particular fatty acids, in a particular way. The thus-conditioned lime is intimately blended with physically-preconditioned moist, hydrocarbon-contaminated soil, under conditions of high shear, the degree of blending being at least near microscopic level. A charge of such blended conditioned lime/soil mixture is conveyed to an enclosed reaction vessel, either continuously or batchwise, and hydration of the lime in the blended conditioned lime/soil charge is carried out. The heat of the hydration reaction is retained within the vessel. Substantially simultaneously, air and/or oxygen-enriched air is introduced into the reaction vessel, together with steam and/or water, thereby to effect a flameless, intermediate-temperature oxidation of the hydrocarbons or of their hydrolysed degradation products. These products are passed through the blended conditioned lime/soil charge at a progressively increasing temperature. Decontami-

nated soil product is discharged from the reaction vessel and may be cooled and then passed through a zone where it may be sprayed with a surfactant. The decontaminated soil product is passed to a blender where it is mixed with sufficient water to provide a substantially dust-free product.

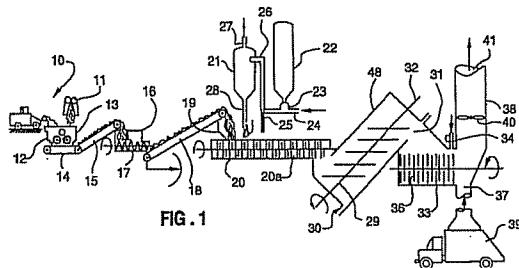


FIG. 1

(i) Technical Field to Which the Invention Relates

This invention relates to a method for the treatment of hydrocarbon-contaminated soil.

(ii) Related Background Art

For some time now, the art has been faced with the problem of the treatment of hydrocarbon-contaminated soils as a result of disposal of industrial materials in soil. Common by-products of plants in which chemicals are made or treated on an industrial scale are aqueous sludge, often containing a high proportion of relatively inert fine particulate materials a variety of reactive materials in sufficiently small concentrations as to make the reclamation thereof uneconomical. Often they are merely pumped on land. The compounds in the sludge solids include common materials, e.g., sulfate ions, calcium ions, aluminum ions, and iron ions or sources thereof as well as water.

The disposition of such sludge has always been a problem. With the increasing awareness of the undesirability of discharging such waste materials into the environment and the resulting governmental regulation of such discharges, the need for a convenient, harmless, and economical way of disposing of such sludge or converting them into a useful product is becoming increasingly apparent. A further incentive is provided by the capital investment and land required for the disposition of such sludge by conventional means, which often include large settling ponds or storage piles.

Another such a problem relates to soil which may have been contaminated through intentional or accidental spills of petroleum oils, hydrocarbon solvents or other, semi-volatile or non-volatile organic materials. Such contaminants may extend over large tracts of land and may directly or indirectly, e.g., through subsequent contamination of an underlying aquifer, constitute an extreme threat to wildlife, vegetation or human health. Conventional methods, e.g., land farming are not very suitable.

Yet another problem relates to oil well sums. Oil well sums are artificial pits used as dump sites for all kinds of liquid and viscous wastes. The physical consistency of the sum varies according to the random materials dumped. Typically, however, in the absence of a water layer, the consistency is pasty. Inasmuch as sums create traps for wild fowl, there is an increasing demand for elimination of sums, especially those not being commercially used. In addition, they are unsightly. The traditional treatment has been to dump and mix dirt into the sum and thereby soak up sufficient of the oil until the dirt-sum material can be moved by conventional equipment. The mixture is then spread to dry. This treatment has not been accept-

able because the mixture bleeds oil and chemicals. Over months and years, this dirt-sum mixture oozes oil and becomes almost as objectionable as the original oil sum. This unsatisfactory type of treatment has called for an improved solution to the ecological problem of sum elimination.

The increasing use of hydrophobic substances, e.g., oils and oily substances, as well as macromolecular substances, has created new problems which arise mainly out of the handling of these substances. Particularly, the use of old oil, heating oils, lubricating oils and diesel fuels often leads, either intentionally or through negligence, and often due to emergency situations, to dangerous contamination of the environment.

There are a number of methods for rendering harmless such oils or oily substances which, in a single phase or in multiple phase systems, entail an endangerment of the environment. For example, oil can be chemically reacted by being burned, for example, or biologically degraded. The combustion method used frequently in combatting oil damage results in considerable air pollution if the burning is performed in the open rather than in expensive combustion apparatus.

The use of adsorbents solves such problem only when the oil can be fixed with them in such a manner that it is chemically unaltered but is encapsulated or otherwise isolated or is accessible to biological degradation and no longer constitutes any danger to the environment. With the known adsorptive agents, e.g., activated charcoal, kieselguhr or bentonite, waste oil, for example, can be adsorptively bound only with difficulty. Large amounts of oil may cement the adsorptive agent, especially in the case of high-viscosity oils, making further processing difficult.

It has furthermore been proposed in various ways to treat porous mineral substances with hydrophobic substances for the purpose of improving their adsorptive characteristics. In this manner hydrophobic waste substances can be preferentially bound, while the water is no longer primarily absorbed. In such adsorptive agents, such as hydrophobized perlite, however, the absorptive capacity is greatly reduced, since the mineral starting material is partially sealed by surface treatment with hydrophobizing substances, so that the inner cavities are no longer accessible.

It is particularly important that the substances which are adsorptively bound by the known processes are so fixed on the adsorptive agent that they no longer constitute any danger to the environment.

In addition to the general, mainly unsatisfactory procedures for the problems of disposal of such wastes discussed above, the patent literature has purported to provide solutions to these problems.

Examples of such solution are provided in: U.S. Patent No. 3,720,609, patented March 13, 1973 by C. L. Smith et al; U.S. Patent No. 4,028,240 patented June 7, 1977 by F. Marchak Jr.; and particularly in U.S. Patent No. 4,018,679 patented April 19, 1977 by F. Boelsing. That Boelsing patent provided a method for rendering an oily waste material harmless by first rendering an alkaline earth metal oxide, e.g., lime, hydrophobic with a surface active agent (e.g., stearic acid), which delayed reaction between the alkaline earth metal oxide and water. The hydrophobic lime mixture was combined with oily waste material, e.g., a sludge or an oil-contaminated soil, and was reacted with water to convert the alkaline earth metal oxide to the hydroxide. This subsequent hydration then alleged to result in an extremely fine and uniform dispersion of the contaminants, hydrated lime and soil. In practice, however, that purpose was not always achieved to its optimum.

Applicant has provided improvements to the above-identified Boelsing patent in U.S. Patent No. 5,290,351 patented March 1, 1994 and U.S. Patent No. 5,374,311 patented December 20, 1994. U.S. Patent No. 5,290,351 provided a hydrophobizing agent comprising a blend which is a liquid at room temperature and is readily atomizable, the blend comprising a mixture of liquid fatty acids having from about 6 to about 12 carbon atoms, and a mixture of glycerides of fatty acids having from about 8 to about 18 carbon atoms.

U.S. Patent No. 5,374,311 provided a composition for rendering a waste substance harmless, the composition comprising a hydrophobizing agent comprising a blend which is liquid at room temperature and is readily atomizable, the blend comprising a mixture of liquid fatty acids having from about 6 to about 12 carbon atoms, and a mixture of glycerides of fatty acids having from about 8 to about 18 carbon atoms, coated on finely ground lime.

(iii) Disclosure of the Invention

The present invention provides a method for rendering harmless an oily, hydrocarbon-contaminated soil by mixing an alkaline earth metal oxide with a surface active agent which temporarily delays reaction between the alkaline earth metal oxide and water until after the alkaline earth metal oxide has interacted with the oily hydrocarbon-contaminated soil, and in which the alkaline earth metal oxide carrying the surface active agent is combined with the oily hydrocarbon-contaminated soil and the alkaline earth metal oxide charged with the oily hydrocarbon-contaminated soil is then reacted with water. The improved method is characterized in that finely-divided lime, either which

has been preheated to a temperature of about 50° to about 80°C, or is heated to such temperature after the treatment, is treated with a hydrophobizing agent, which is a clear, readily-atomizable liquid at room temperature and which consists essentially of a fatty-acid having of from about 6 to about 12 carbon atoms therein, thereby to provide conditioned lime in which the finely-divided lime is uniformly-coated with the hydrophobizing agent. The conditioned lime is then blended, preferably in a ratio of from about 1:6 to about 1:1, with physically-preconditioned moist, hydrocarbon-contaminated soil, under conditions of high shear, the degree of blending being at least near microscopic level, thereby providing blended, conditioned lime/soil. A charge of such blended, conditioned lime/soil is conveyed to an enclosed reaction vessel, and either that charge is moved continuously slowly through the enclosed reaction vessel, or that charge is fed batchwise to the enclosed reaction vessel to retain the charge in the enclosed reaction vessel for a pre-determined period of time. In either case, the residence time in the enclosed reaction vessel is from about 10 to about 45 minutes. Air, and/or oxygen-enriched air, is substantially simultaneously introduced into the reaction vessel together with steam and/or water, thereby to effect a flameless, intermediate-temperature oxidation of at least one of the hydrocarbons and hydrolysed degradation products of the hydrocarbons and thereby contacting organic constituents and residues of incomplete oxidation products of the oxidation with the conditioned lime/soil charge at a progressively increasing temperature which is adequate for completion of all hydration, hydrolysis and oxidation reactions, whereby the heat of the hydration reaction is retained within the enclosed reaction vessel. Decontaminated soil product is then discharged from the enclosed reaction vessel by passing the decontaminated soil product, in dry, dusty, hydrophobic form through a zone where it may be sprayed with a surfactant, thereby to provide treated decontaminated soil product. The treated decontaminated soil product is passed to a blender, where it is mixed with water in an amount ranging from about 5% to about 25%, based on the quantity of the treated decontaminated soil product, thereby to provide a substantially dust-free product.

The present invention also provides an agent for above-described use as a conditioned lime. The agent is characterized in that it comprises a mixture of liquid fatty acids having from about 6 to about 12 carbon atoms, which is uniformly-coated on finely-ground lime. The amount of the liquid fatty acid mixture is sufficiently fully to coat the finely-ground lime. Preferably, such amount is from about 0.5% to about 2.5% by weight of the composition, and still more preferably is about 1.0%.

By one feature of this invention, the hydrocarbon contaminated soil is moist and has a maximum grain size less than about 5 cm.

By yet another feature of this invention, the fatty acid hydrophobizing agent comprises a saturated fatty acid of low-to-moderate carbon chain length and high acid number, e.g., where the liquid fatty acids have from about 6 to about 12 carbon atoms, and where the acid number is about 355 to about 369, and most preferably where the fatty acid hydrophobizing agent comprises a mixture of a preponderant amount of caprylic acid and capric acid.

The size of the finely-divided lime is from about 3 to about 5 mesh/lineal cm with 2.0 mm sieve openings.

Broadly speaking, the mixture of liquid fatty acids comprise a preponderant amount of caprylic acid and capric acid. Preferably, such mixture of liquid fatty acids comprises caproic acid, caprylic acid, capric acid, and lauric acid. Still more preferably, such mixture of liquid fatty acids comprise about 1% caproic acid; about 55% caprylic acid; about 42% capric acid; and about 2% lauric acid.

The mixture of liquid fatty acids may be those derived from coconut oil, i.e., coconut acid, e.g., principally lauric acid, and also caprylic, capric, myristic, palmitic, stearic, oleic and linoleic acids. One such coconut acid comprises caprylic acid, about 8.0; capric acid, about 7.0; lauric acid, about 48.0; myristic acid, about 17.5; palmitic acid, about 8.2; stearic acid, about 2.0; oleic acid, about 6.0; and linoleic acid, about 2.5. Another such coconut acid comprises lauric acid, about 47%; myristic acid, about 19%; palmitic acid, about 9%; oleic acid, about 7%; stearic acid, < about 3%; and other lower molecular weight fatty acids, > about 15%.

Another such mixture of liquid fatty acids may be those derived from babassu oil, i.e., babassu acid, e.g., principally lauric acid as well as caprylic acid, capric acid, myristic acid, palmitic acid and oleic acid. One such babassu acid comprises: caprylic acid, about 6.5%; capric acid, about 2.7%; lauric acid, about 45.8%; myristic acid, about 19.9%; palmitic acid, about 6.9%; and oleic acid, about 18.1%.

Yet another such mixture of liquid fatty acids may be those derived from palm kernel oil, i.e., palm kernel acid, e.g., principally lauric acid, as well as caprylic acid, capric acid, myristic acid, palmitic acid, stearic acid, oleic acid and linoleic acid. One such palm kernel acid comprises: caprylic acid, about 3.0%; capric acid, about 3.0%; lauric acid, about 52.0%; myristic acid, about 15.0%; palmitic acid, about 7.5%; stearic acid, about 2.5%; oleic acid, about 16.0%; and linoleic acid, about 1.0%.

In one alternative feature of the invention, the method incorporates the step of continuously feeding the blended conditioned lime/soil charge, whereby the blended conditioned lime/soil charge moves slowly through the reaction vessel for a residence time of about 10 to about 45 minutes. In another alternative feature of the invention, the method incorporates the step of batchwise feeding of the blended conditioned lime/soil charge, the blended conditioned lime/soil charge being retained in the reaction vessel for a predetermined period of time, for a residence time of about 10 to about 45 minutes.

In still another feature of the invention, the direction of flow of the introduced air is co-current to the direction of flow of the blended conditioned lime/soil charge through the reaction vessel.

In yet a further feature of the invention, the surfactant comprises an aqueous solution of sodium hydroxide.

In a still further feature of the invention, the decontaminated soil is cooled to a suitable low temperature, e.g., lower than about 100 °C, before being sprayed with the surfactant.

In another feature of the invention, the intimate blending is provided by an apparatus capable of imparting sufficient shear and mixing action. The conditions of high shear should be similar to those obtained with the aid of a concrete mixer, e.g., the one known by the trade-mark NIKKO MIXER, a product of Nikko Co., Ltd. in Tokyo, Japan. The degree of dispersion must be at least near microscopic level.

In the method of the present invention, the surfactant may comprise commercial or industrial soaps or detergents, at concentration ranging from about 30% to about 80% by weight, or it may comprise an aqueous solution of sodium hydroxide, e.g., where concentration of the sodium hydroxide is from about 5% to about 10% by weight.

The method of the present invention may further include the steps of cooling the decontaminated soil to a temperature below about 100 °C and then spraying with the surfactant.

In the method of the present invention, the hydrophobizing agent is preferably prepared by feeding the mixture of liquid fatty acids as described above to a spray nozzle, and that mixture of liquid fatty acids is sprayed into a rising air stream carrying fine lime particles. Preferably, the pressure gradient across the spray nozzle is from about 520 mm Hg to about 1560 mm Hg. Preferably also, the air flow velocity is within the range of about 910 M/min. to about 1820 M/min.

(iv) Effects of the Invention in the Context of the Background Art

The background art still did not provide a process for treating hydrocarbon-contaminated soils in a manner which would result in the destruction of the hydrocarbon and the fixation and stabilization of all noxious contaminants. Accordingly, the advantageous effects of the present invention are that it provides a method that requires all organic constituents, including chlorinated vapours, pyrolysis products, and other solid, liquid and gaseous residues of incomplete oxidation, to pass through a blended conditioned lime/soil bed at progressively increasing temperatures before emerging from the reactor. As a consequence, the complete pyrolysis, dechlorination and ultimate oxidation of the organic components is absolutely assured. The present invention now provides a novel solution to the technical problem of treating hydrocarbon contaminated soils in a manner which will result in the destruction of the hydrocarbon and the fixation and stabilization of noxious contaminants.

As a consequence of a complex array of chemical reactions, including hydration, hydrolysis, pyrolysis and oxidation, the organic molecules are systematically converted to innocuous residues, e.g., water and carbon dioxide and, depending upon the original composition of the contaminants, a variety of acid gases which are subsequently trapped within the solid mixture as common calcium salts.

The combined impact of, first, limiting the volume of inert gas introduced into the system, then, of attaining dechlorination and decomposition of all organic contaminants and, finally, of scrubbing virtually all toxic or otherwise undesirable reaction products from the vapour phase, is the production of a relatively small quantity of a benign gaseous effluent stream which requires no further attention or treatment.

The present inventive method tends to be largely energy self-sufficient, since all of the reactions, including lime hydration, pyrolysis and oxidation, are rather strongly exothermic. Thus, a significant measure of the energy required to elevate the temperature of the reaction mixture to that required for hydration, pyrolysis and, ultimately oxidation is internally available.

It has now been found that a particularly-recited fatty acid hydrophobizing agent is sufficient to achieve the desired results and effects, provided that the combined lime and fatty acid is warmed to a temperature in the range of about 50 °C to about 80 °C. It has now been found, according to the present invention, that the determining characteristic of the fatty acid hydrophobizing agent is its hydrocarbon chain length, e.g., from C₆ - C₁₂, i.e.,

from C₈ - C₁₀, and its acid number, e.g., from about 355 - 369, since these properties determine the extent of masking of the lime particle surface and the rate of water penetration and breakdown of the mask. More specifically, the most desirable combination of fatty acid properties is a saturated molecular structure of low to moderate carbon chain length and a high acid number.

In the development of the present invention to provide additional advantageous effects of optimizing the economics and operational simplicity of the process, a number of single, commercially-available fatty acids were evaluated in the hope that a suitable substitute might be found for the hydrophobizing agent of Applicant's prior patents which was a rather costly blend of fatty acids and coconut oil. The basis for the development was the combined ability of the hydrophobizing agent, when applied at equivalent concentration levels in the range of about 0.5% to about 2.0%, adequately to delay the onset of lime hydration to permit thorough mixing of the lime with the soil and to achieve a comparable final temperature of the mixture at the end of the first, hydration stage of the process.

One of the advantageous effects of the present invention is that it provides a method involving blending of the contaminated soil with water and chemically preconditioned lime, whereby, when the resulting mixture is conveyed through a specified system in a controlled environment of oxygen or oxygen enriched air and water or steam, it would be subjected to a sequence of precisely programmed thermal treatments to decontaminate the soil.

The basis for the successful operation of the present invention is the ability of the hydrophobizing agent, when applied at equivalent concentration levels in the range of about 0.5% to about 2.0% by weight, both adequately to delay the onset of lime hydration to permit thorough mixing of the lime with the soil and also to achieve a comparable final temperature of the mixture at the end of the first, hydration stage of the process.

It has been found, by the present invention, that a liquid, easily-vaporizable fatty acid hydrophobizing agent, e.g., that known by the Trade Mark INDUSTRENE™ 365, is sufficient to achieve the desired characteristics, provided that the combined lime and fatty acid is warmed to a temperature in the range of about 50 °C to about 80 °C. Accordingly, the effects of the invention are achieved when the determining characteristic of the fatty acid hydrophobizing agent is its hydrocarbon chain length, e.g., from C₆ - C₁₂, i.e., from C₈ - C₁₀, and its acid number, e.g., from about 355 to about 369, since these properties determine the extent of masking of the lime particle surface and

the rate of water penetration and breakdown of the mask. More specifically, the most desirable combination of fatty acid properties is a saturated molecular structure of low to moderate carbon chain length and a high acid number.

In providing the conditioned lime, the amount of the hydrophobizing agent is selected to be sufficient fully to coat the finely divided lime particles. In practice therefore, this would range from about 0.5% to about 2.5% by weight, with the optimum amount being about 1.0%. The size of the finely-divided lime is generally within the range of about 3 to about 5 mesh/lineal cm with 2 mm sieve openings to sub-micron sizes.

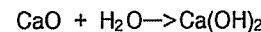
The lime is mixed with the fatty acid in the manner which will be described hereinbelow. The preferred method of providing the conditioned lime comprises feeding of the above-described hydrophobizing agent to a spray nozzle, and spraying such hydrophobizing agent into a rising air stream carrying fine lime particles. The pressure gradient across the spray nozzles should be about 520 m/Hg to about 1560 m/Hg. The velocity of upward flow of air is within the range about 910 to about 1820 M/mm.

It has further been found, according to the present invention, that the addition of sodium hydroxide to at least one of the soil to be treated and the conditioned lime/soil mixture at levels of up to about 1.0% of the quantity of lime, is effective in regulating the length of the induction period preceding lime hydration.

By the present invention, a novel multi-step method has been provided for the treatment of hydrocarbon-contaminated soil through effective chemical hydrolysis and/or oxidation of the hydrocarbon contaminants. In the first step of the procedure, the lime is conditioned with the fatty acid hydrophobizing agent, in accordance with the method described above, then heated to about 50°C to about 80°C. An appropriate quantity of the thus-conditioned lime, ranging, based on the mass of soil, from about 15% to about 100% as dictated by the quantity of moisture in the feed, the nature of the soil and the type and quantity of the hydrocarbons present (determined through laboratory testing), is intimately blended with physically-preconditioned, moist, hydrocarbon-contaminated soil, which may or may not be further contaminated with noxious heavy metals. While a wide variety of devices capable of imparting the requisite shear and mixing action to the ingredients are commercially available, it is imperative that the degree of dispersion achieved be at the near microscopic level. This provides a blended soil charge.

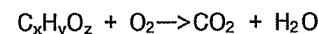
The blend of conditioned lime/soil is, then, transferred to a reaction vessel in either continuous or batchwise fashion. If it is fed in a continuous

fashion, the blended conditioned lime/soil charge moves slowly through the reactor. If it is fed batchwise, the blended conditioned lime/soil charge is retained for a predetermined period of time which may range from about 10 minutes to about 45 minutes but which is adequate for completion of all hydration, hydrolysis and oxidation reactions. In either procedure, the reactor design is such that the heat generated during the hydration of the lime in accordance with the reaction:



is contained within the blended conditioned lime/soil charge, thereby causing the temperature to rise to a level at which hydrolysis of the hydrophobizing agent and, possibly certain of the hydrocarbon contaminants, is initiated.

Air, or oxygen-enriched air, combined with water and/or steam where required by the chemical processes, is also introduced into the reactor to effect a flameless, intermediate temperature oxidation of the original hydrocarbons or the hydrolysed degradation products of such hydrocarbons. The air or oxygen enriched air flow rate must be sufficiently high to provide an excess of about 50% to about 100% of the stoichiometric oxygen requirements of the oxidation reactions while being limited to a level which will minimize the heat removal from the reaction mixture. These conflicting requirements may be accommodated through adjustments in the quantity of steam supplied to the reactor and the degree of oxygen enrichment of the air. The oxidation reactions may be represented generically as:



In the continuous method embodiment, the direction of flow of the air and the blended conditioned lime/soil charge in the reactor is co-current. This ensures that any vaporized hydrocarbons, or incompletely hydrolysed/oxidized hydrocarbon degradation products, are carried from the region of high concentration obtaining near the blended conditioned lime/soil charge influent port to a region of low concentration and higher temperature nearer the exit, thereby providing an enhanced opportunity for further reaction.

The decontaminated soil product, which is normally very dry, dusty and extremely hydrophobic, leaves the reactor and, if necessary is pre-cooled, and, also if necessary, then passes through a spray of surfactant en route to another blender (e.g. a conventional pug mill) where it is mixed with a sufficient quantity of water to permit dust-free transfer to the final disposal site and/or compaction into a dense, stable monolith which, upon curing,

provides virtually permanent encapsulation of any inorganic or surviving, trace organic residues.

If it is used, the surfactant or wetting agent may be any of a number of commercially available long chain organic molecules, e.g. industrial or domestic soaps and detergents. However, it is preferable that this agent be a solution of about 5% sodium hydroxide in water which is sprayed onto the dry reactor effluent in sufficient volume to ensure the desired water-wetting and compaction qualities of the final product from the process. The actual quantity will be determined by the nature of the soil, the quantity of lime employed, etc. and will range from about 1% to about 10% of the weight of the process product.

According to the present invention, the hydrophobizing agent to condition the lime comprises certain liquid saturated fatty acids, [e.g., those derived from coconut oil, (namely coconut acid), babassu oil, (namely, babassu acid), or palm kernel oil, (namely, palm kernel acid)]. Since the fatty acids are a liquid at room temperature, they may be very easily and uniformly combined with the fine-ground lime, thereby uniformly to coat the surface of the lime. This procedure preferably is accomplished with the aid of a spray nozzle which introduces the hydrophobizing agent into a rising air stream carrying the fine-ground lime particles.

The general composition of fatty acids in coconut acid is as follows: caprylic, about 8.0; capric, about 7.0; lauric, about 48.0; myristic, about 17.5; palmitic, about 8.2; stearic, about 2.0; oleic, about 6.0 and linoleic, about 2.5. In one preferred coconut acid, the approximate composition of the fatty acids is as follows: lauric acid, about 47%; myristic acid, about 19%; palmitic acid, about 9%; oleic acid, about 7%; stearic acid, < about 3% and other (lower molecular weight fatty acids), > about 15%.

The approximate composition of fatty acids in babassu acid is as follows: caprylic, about 6.5; capric, about 2.7; lauric, about 45.8; myristic, about 19.9; palmitic, about 6.9; and oleic, about 18.1.

The approximate composition of fatty acids in palm kernel acid is as follows: caprylic, 3.0; capric, about 3.0; lauric, about 52.0; myristic, about 15.0; palmitic, about 7.5; stearic, about 2.5; oleic, about 16.0; and linoleic, about 1.0.

A preferred liquid fatty acid mixture is that known by the trademark INDUSTRENE 365_{TM} of Hunko Products Division, National Dairy Products Corporation, which is a mixture of caprylic acid and capric acid.

The desired characteristic of the hydrophobizing agent to condition the lime is that it virtually inhibit the lime hydration until the lime is mechanically blended with the contaminated soil with the aid of vigorous stirring. It is preferably allowed to remain undisturbed. Then the reaction should occur

at a high rate as indicated by a rapid and extensive rise in temperature. This behaviour is seen to be optimum when the concentration of the hydrophobizing agent in the conditioned lime is within the range of about 0.5% and about 2.5%, with the optimum performance noted at approximately 1.0%.

The hydrophobizing agent also acts as an activator/initiator in the present inventive method for rendering waste substances harmless.

In the novel method of the present invention, as will be described in greater detail hereinafter, at some point during the lime hydration reaction, the hydrophobizing agent begins to react with the conditioned lime. Coupled with the destruction of the lime is the release of sufficient heat to raise the temperature of the mass significantly above about 100 °C, the boiling point of water. Temperatures in excess of about 150 °C may be achieved. At this temperature, hydration, which clearly involves water as a reactant, must soon cease and hydrolysis of the conditioned lime takes place. In mixtures of fatty acid conditioned lime (according to the present invention) and hydrocarbon contaminated soil, temperatures in excess of about 400 °C have been observed. In fact, in some instances temperatures may reach as high as about 700 °C. Because of these high temperatures, the charge may have to be cooled to a temperature below about 100 °C before, if required, the decontaminated soil is sprayed with the suitable wetting agent, as will be described hereinafter. This behaviour of the hydrophobizing agent as an activator/initiator contributes to the chemical destruction of the hydrocarbon contaminants originally present in the waste soil and is an important mechanism in the operation of the above-described novel method.

(iv) Brief Description of the Drawings

In the accompanying drawings,
Fig. 1 is a schematic process flow sheet of a system adapted to carry out the method of one embodiment of this invention;
Fig. 2 is a schematic longitudinal section of a laboratory hydrocarbon test furnace;
Fig. 3 is a graph showing a typical reactor temperature profile;
Fig. 4 is a schematic longitudinal section of a laboratory dechlorination furnace; and
Fig. 5 is another graph showing a typical furnace temperature profile.

(v) Description of Special Embodiments

As seen in Fig. 1, the contaminated soil is removed from the area of contaminants and is fed, by a front-loader 10 either to a jaw crusher 11 or a

roll crusher 12 to a hopper 13 provided with a conveyor system 14. Conveyor system 14 feeds an inclined ramp portion 15 leading to a hopper 16 provided with a feed rate control screw soil feeder 17, driven by means (not shown) in the direction shown by the arrow. Screw soil feeder 17 feeds soil to a second weigh-type conveyor system 18 where the soil is fed through a blender hopper 19 to a blender 20 provided with suitable means 20a for blending.

The lime is activated, in the manner previously described, in the activation apparatus 21. Lime is stored in a lime storage vessel 22 where it is fed from a rotary valve 23 at the bottom of the lime storage vessel 22, and is carried by air, supplied through line 24, mixed with fatty acid, and heated, (as previously described) in line 25 to combined inlet line 26 to activated lime storage and feed apparatus 21. Air is exhausted through vent 27. The conditioned lime is discharged via outlet 28 through the blender hopper 19 to the blender 20. From the blender 20, the blended conditioned lime/soil charge is fed to an inclined reactor 48 provided with an upwardly feeding screw conveyor 29 rotated by motor means (not shown) in the direction shown. Oxidizing air together with water and/or steam as determined by the stoichiometry and thermal requirements of the chemical reactions is fed co-currently to the flow of the charge through air inlet 30 to the inclined reactor 48.

At the exit 31 from the inclined reactor 48, the decontaminated soil may be cooled to a suitable low temperature, e.g., lower than about 100°C, and then, if necessary, is sprayed with a suitable wetting agent, as previously described, through spray nozzle 32 and is fed to a pug mill 33. At the pug mill 33, the decontaminated soil is wetted with water through inlet 34, and is discharged by horizontal screw conveyor 36, rotated by motor means (not shown) in the direction shown to the outlet 37 of a discharge tower 38 to a suitable truck 39.

The discharge tower 38 includes an internal fan 40 which forces air outwardly to 41 to a cleanup zone (not shown) and maintains a slight negative pressure in the reactor of approximately 1 cm to 3 cm water vacuum to minimize fugitive emissions.

The decontaminated soil may be fed to a compaction zone (not shown) and/or to landfill.

The following experiments are presented in order to show the solving of the above-described technical problems by this invention.

Experiment A - Destruction of Hydrocarbons

A test apparatus for the destruction of hydrocarbons is shown in Fig. 2, where the laboratory furnace 200 includes a tube 201 provided with a soil/lime packing 202, namely lime conditioned with

a fatty acid according to the teachings of the present invention. A heating coil 203 is provided surrounding the tube and has electrical lead lines 204 to provide electrical energy to the heating coil 203.

The tube 201 is provided with an oxygen inlet tube 205 and a concentric hydrocarbon inlet tube 206. An outlet tube 207 leads the gas phase to suitable analysis.

The test procedure consisted of the following steps:

- a) The 24 inch long by 5/8 inch internal diameter quartz tube reactor was packed with a sufficient charge of a 35% mixture of lime in sandy soil to provide an active (hot zone) bed height of approximately 16 inches;
- b) When the reactor attained the desired operating temperatures, as depicted by the typical temperature profile shown in Fig. 3, air, oxygen-enriched air or pure oxygen, at some preselected flow rate between 50 ml per minute and 900 ml per minute, was introduced near the bottom of the packed column;
- c) Subsequently, methane, which, like benzene, is extremely refractory to oxidation and displays a high autoignition temperature when compared with other hydrocarbons, was injected into the hot zone of the refractor at approximately 4 inches above the bottom of the column. The flow rates of methane varied from 6 ml per minute to 70 ml per minute, thereby yielding an equivalent inlet gas composition ranging from 2% to 27%. It is noteworthy that the latter figure pertains to an experiment involving this highly combustible blend of methane in pure oxygen. Many other experiments were conducted employing oxygen at similarly high concentrations of methane;
- d) Temperature profiles within the reactor were monitored with the aid of a traversing thermocouple throughout the course of the experiment. This procedure permitted both determination of the temperature required to achieve the desired level of oxidation and detection of any points of ignition which invariably signifies the undesirable onset of high temperature combustion;
- e) The gas stream emerging from the top of the reactor was transported successively through: (i) a condenser - to cool the gas and to remove the water resulting from the oxidation of the methane, (ii) a calcium chloride dryer - to remove the last traces of water vapour, (iii) a spectroscopic analyzer to determine the residual concentration of any surviving hydrocarbon, and (iv) an oxygen analyzer - to determine and permit control of the excess oxygen level;

(f) Gas samples were also taken for chromatographic analysis to monitor any evolution of carbon dioxide and to determine methane residuals when the concentration of this component in the effluent exceeded the operating range of the spectroscope.

The results of the experiments conducted with this apparatus confirmed that, within the packed bed, a significant degree of non-combustive oxidation of methane was achieved, in air, at temperatures in the order of 570°C to 590°C. This temperature was progressively reduced to approximately 540°C as the oxygen concentration of the enriched air was increased toward 100%. Due to methane dilution arising both from its depletion and the production of water vapour by the oxidation reaction, total destruction of the methane was achieved only by increasing the temperature to 700°C. In fact, at this temperature, the quantity of methane surviving the reaction was below the detection limit of 2 ppm to 5 ppm in the effluent stream.

These findings suggests that the ideal reactor would permit manipulation of both the bed temperature and the temperature profile along its length. Prior to depletion of the lime in the upper regions of the static bed, the carbon dioxide formed by the oxidation reaction was absorbed in the form of calcium carbonate and the gas phase concentration was reduced to below detectable levels. Despite the fact that the methane concentrations in the air and/or oxygen feed stream far exceeded the lower explosion limit of this hydrocarbon, no detonation ever occurred in the reactor. This confirmed the inherent stability and safety of the method of the present invention. While it is not desired to be limited to theoretical consideration, it is believed that this extremely desirable characteristic likely arises from the fact that the thermal capacity of the bed material and the very short flame path length between the particles comprising the bed prevents either an unrestrained rate of increase in temperature or the propagation of a flame front.

EXPERIMENT B - Destruction of Chloro-Organic Compounds

The apparatus employed in the performance of these experiments for the destruction of chloro-organic compounds is illustrated in the schematic representation in Fig. 4. As seen in Fig. 4, the test furnace 400 comprises a tube 401 provided with a soil/lime packing 402 in a reactor section 403 which is equivalent to that shown in Fig. 2. A heating coil 404 provided with electric line 405 surrounds the packed part of the tube to provide the reactor section 403. The upper, unpacked part

of the tube 401 provides an afterburner section 406. It, too, is provided with a heating coil 407 provided with electrical lead lines 408 to provide electrical energy to the heating coil 407.

An oxygen inlet 409 discharges into a lower portion of packed bed 402, and a chlorinated hydrocarbon inlet 410 discharges into a mid portion of the packed bed 402. An outlet tube 411 leads a gas phase to an absorber.

The reactor consisted of a 30 inch long, 5/8 inch internal diameter alumina tube suspended in a two zone furnace wherein the temperature of each zone was independently controllable. The lower zone was equipped with an oxygen injection port near the base and a chlorinated organic (trichlorobenzene) injection port at point within the heated region. This zone contained lime/soil packing with an active depth of approximately 8 inches and, as illustrated in the graph of Fig. 5, displayed a temperature gradient across its length which increased from 400°C at the point of injection of the chlorinated organic to 750°C at the upper extremity of the bed, thereby ensuring immediate vaporization then progressive total destruction of the entering contaminant.

The upper zone of the reactor was maintained at the substantially higher average temperature of approximately 1250°C. This ensured that any chlorinated residues or noxious by-products which might escape from the first zone would encounter temperatures and retention times which, in the oxygen rich atmosphere obtaining, would experience complete oxidation to carbon dioxide, water and hydrogen chloride.

The test procedure consisted of the following steps:

- a) Under conditions of a steady oxygen flow rate of 20 ml per minute through the packing, the two zones of the reactor were preheated for the period required to attain an overall constant temperature gradient similar to that exhibited in Fig. 5;
- b) A quantity of trichlorobenzene equal to approximately 15% of the mass of active packing in the reaction zone was then injected through the appropriate port at a steady rate of approximately 2 ml per hour with the aid of a syringe pump;
- c) The gas stream evolving from the upper zone was conducted through and intimately contacted with a 5% solution of sodium hydroxide to achieve absorption of any hydrogen chloride which had escaped from the reactor bed or the high temperature oxidation zone;
- d) Upon completion of the reaction period, the bed material was removed from the reactor column and extracted with water. Since it was reasonably assumed that dechlorination would

necessarily result in the production of hydrogen chloride, which would subsequently react with the lime in the bed to form calcium chloride, the extract was then analyzed for chloride ion to determine the extent, if any, of such dechlorination within the lime/soil bed;

e) The sodium hydroxide absorber solution was also examined for the presence of chloride ion to establish the degree to which chlorinated by-products had survived the conditions in the bed.

The several experiments performed with the dual zone reactor confirmed that since no detectable quantity of chloride ion appeared in the sodium hydroxide solution, complete dechlorination of trichlorobenzene was achieved at the temperature levels imposed on the bed. Substantial quantities of soluble chloride ion were extracted from the bed material. However, in the initial tests, the material balance indicated a recovery of only some 70% of the chlorine associated with the injected trichlorobenzene.

It was noted that the temperature at, and for an appreciable distance beyond the point of injection of the trichlorobenzene, while above the boiling point of that compound, was, at 450 °C, decidedly below the temperature required for its complete pyrolysis and oxidation. While it is not desired to be limited by theory, it was, therefore, assumed that the missing chloride ion was a reflection of the reformation of some of the trichlorobenzene into high boiling point chloro-organic residues which remained adsorbed to the column packing.

In subsequent tests, the lower zone temperature of the column at the end of the trichlorobenzene injection period was increased to approximately 620 °C in the vicinity of the injection nozzle and maintained at that level for 15 minutes. The subsequent 100% recovery of chloride ion from the packing material both appeared to confirm the foregoing assumption and established the method of the present invention as a viable technique for the destruction of chlorinated organic contaminants.

(vi) Industrial Applicability

Extensive laboratory studies (as described above) have confirmed that the method of the present invention is capable of achieving substantially complete destruction of a wide spectrum of hydrocarbon species, ranging from methane to high molecular weight mineral oil distillates, through a combination of hydrolysis, pyrolysis and oxidation. Moreover, provided that appropriate control and discipline of the reaction mechanism is maintained, it is possible to effect this oxidation without incurring the conditions of high temperature normally associated with conventional incineration. More specifically, temperatures in the vicinity of

about 700 °C have proven to be adequate for the removal of all measurable traces of methane from the gaseous reactor effluent stream. Complete dechlorination and destruction of highly refractory polychlorinated aromatics, e.g., trichlorobenzene (and most likely PCB's) without the production of undesirable polyaromatic dioxin and furan byproducts was achieved. Virtual elimination of noxious chemical emissions, including residual hydrocarbons, chlorine and even carbon dioxide was achieved. Consequently, if the oxidation is accomplished with the aid of relatively pure oxygen, the total gaseous effluent from the process will be minimal, comprising only the nitrogen introduced with the feed, traces of carbon dioxide and uncondensed water vapour.

Due to the relatively low temperatures encountered by the blended conditioned lime/soil charge as it proceeds through the apparatus in carrying out the method, the extent of heavy metal vaporization (other than that of mercury) and the degree of nitrogen fixation should be negligible.

The method of the present invention represents a new approach to the remediation of soils and other granulated substrates contaminated with hydrocarbons or other hazardous organic species, e.g., polychlorinated biphenyls, pentachlorophenol and a host of other widespread, durable and pernicious environment pollutants, and comprises a truly viable and attractive alternative to the only current, proven method of choice, namely, incineration.

The unique feature of the present invention, and that which distinguishes it from other, less successful lime-based dechlorination procedures, is that, in the prior art procedures, the method of heating the contaminated soil/lime mixture and the configuration of these systems invariably caused the organic constituents to be expelled from the reaction zone through evaporation before attaining an adequate duration of exposure to the necessary decomposition temperatures.

Claims

- 45 1. A method for rendering harmless an oily hydrocarbon-contaminated soil by mixing an alkaline earth metal oxide with a surface active agent which temporarily delays reaction between the alkaline earth metal oxide and water until after the alkaline earth metal oxide has interacted with the oily hydrocarbon-contaminated soil, combining the alkaline earth metal oxide carrying the surface active agent with the oily hydrocarbon-contaminated soil and reacting the alkaline earth metal oxide charged with the oily hydrocarbon-contaminated soil with water characterized in that:

a) finely-divided lime, which is either preheated to a temperature of about 50 °C to about 80 °C, or is so heated after treatment, is treated with a hydrophobizing agent, which is a clear, readily-atomizable liquid at room temperature and which consists essentially of a mixture of fatty acids having from about 6 to about 12 carbon atoms therein, thereby to provide conditioned lime in which the finely-divided lime is uniformly-coated with the hydrophobizing agent;

b) said conditioned lime is blended, in a ratio of from about 1:6 to about 1:1, with physically-preconditioned moist, such hydrocarbon-contaminated soil, under conditions of high shear, the degree of blending being at least near microscopic level, thereby providing blended, conditioned lime/soil;

c) a charge of such blended, conditioned lime/soil is conveyed to an enclosed reaction vessel, and either said charge is moved continuously slowly through said enclosed reaction vessel, or said charge is fed batch-wise to said enclosed reaction vessel in either case, the residence time in said enclosed reaction vessel being from about 10 to about 45 minutes, thereby carrying out hydration of said lime in said blended conditioned lime/soil charge, and air, and/or oxygen-enriched air, is substantially simultaneously introduced into said reaction vessel together with steam and/or water, thereby to effect a flameless, intermediate-temperature oxidation of at least one of said hydrocarbons and hydrolysed degradation products of said hydrocarbons and thereby contacting organic constituents and residues of incomplete oxidation products of said oxidation with said conditioned lime/soil charge at a progressively increasing temperature, which is adequate for completion of all hydration, hydrolysis and oxidation reactions, and whereby the heat of said hydration reaction is retained within said enclosed reaction vessel;

d) decontaminated soil product is discharged from said enclosed reaction vessel by passing said decontaminated soil product, in dry, dusty, hydrophobic form through a zone where it may be sprayed with a surfactant, thereby to provide treated decontaminated soil product; and

e) said treated decontaminated soil product is passed to a blender, where it is mixed with water in an amount ranging from about 5% to about 25%, based on the quantity of said treated decontaminated soil product,

thereby to provide a substantially dust-free product.

2. The method of claim 1 characterized by the step of incorporating up to about 1% by weight of sodium hydroxide, based on the weight of lime, into said physically-preconditioned, moist, hydrocarbon-contaminated soil.
3. The method of claim 1 or claim 2 characterized in that said oily, hydrocarbon contaminated soil has a maximum grain size less than about 5 cm.
4. The method of claim 1, or claim 2, or claim 3, characterized in that the direction of flow of said introduced air or oxygen-enriched air is co-current to the direction of flow of said blended conditioned lime/soil charge through said reaction vessel.
5. The method of claim 4 characterized in that said introduced air or oxygen-enriched air flows from the point of introduction into the reaction vessel to the point of discharge from the reaction vessel.
6. The method of any one of claims 1 to 5 inclusive, characterized in that said surfactant comprises commercial or industrial soaps or detergents at concentration ranging from about 30% to about 80% by weight.
7. The method of any one of claims 1 to 6 inclusive, characterized in that said surfactant comprises an aqueous solution of sodium hydroxide.
8. The method of claim 7 characterized in that the concentration of said sodium hydroxide is from about 5% to about 10% by weight.
9. The method of any one of claims 1 to 8 inclusive, characterized in that the steps of cooling said decontaminated soil to a temperature below about 100 °C and the spraying with said surfactant.
10. For use as a conditioned lime in the method of any one of claims 1 to 8 inclusive, an agent consisting of a blend which is liquid at room temperature and is readily atomizable, said blend being characterized by: a mixture of liquid fatty acids having from 6 to 12 carbon atoms, said blend being uniformly coated on finely-ground lime.

11. The agent of claim 10 characterized in that the amount of said fatty acids is sufficiently fully to coat the finely-ground lime.

12. The agent of claim 10 characterized in that the amount of said fatty acids is present in an amount of from about 0.5% to about 2.5% by weight of the composition. 5

13. The agent of claim 12 characterized in that the amount of said fatty acids is about 1.0%. 10

14. The agent of any one of claims 10 to 13 inclusive, characterized in that size of the finely-divided lime is from about 3 to 5 mesh/lineal cm with 2.0 mm sieve openings. 15

15. The agent of any one of claims 10 to 14 inclusive, characterized in that said liquid mixture of fatty acids comprise a preponderant amount of caprylic acid and capric acid. 20

16. The agent of any one of claims 10 to 14 inclusive, characterized in that said liquid mixture of fatty acids comprises caproic acid, caprylic acid, capric acid, and lauric acid. 25

17. The agent of any one of claims 10 to 14 inclusive, characterized in that said liquid mixture of fatty acids comprise about 1% caproic acid; about 55% caprylic acid; about 42% capric acid; and about 2% lauric acid. 30

18. The agent of any one of claims 10 to 14 inclusive, characterized in that said liquid mixture of fatty acids comprises caprylic acid, about 8.0; capric acid, about 7.0; lauric acid, about 48.0; myristic acid, about 17.5; palmitic acid, about 8.2; stearic acid, about 2.0; oleic acid, about 6.0; and linoleic acid, about 2.5. 35

19. The agent of any one of claims 10 to 14 inclusive, characterized in that said liquid mixture of fatty acids comprises lauric acid, about 47%; myristic acid, about 19%; palmitic acid, about 9%; oleic acid, about 7%; stearic acid, < about 3%; and other lower molecular weight fatty acids, > about 15%. 40

20. The agent of any one of claims 10 to 14 inclusive, characterized in that said liquid mixture of fatty acids comprises principally lauric acid as well as caprylic acid, capric acid, lauric acid, myristic acid, palmitic acid and oleic acid. 50

21. The agent of any one of claims 10 to 14 inclusive, characterized in that said liquid mixture of fatty acids comprises caprylic acid, 55

about 6.5%; capric acid, about 2.7%; lauric acid, about 45.8%; myristic acid, about 19.9%; palmitic acid, about 6.9%; and oleic acid, about 18.1%.

22. The agent of any one of claims 10 to 14 inclusive, characterized in that said liquid mixture of fatty acids comprises principally lauric acid, as well as caprylic acid, capric acid, lauric acid, myristic acid, palmitic acid, stearic acid, oleic acid and linoleic acid.

23. The agent of any one of claims 9 to 13 inclusive, characterized in that said liquid mixture of fatty acids comprises caprylic acid, about 3.0%; capric acid, about 3.0%; lauric acid, about 52.0%; myristic acid, about 15.0%; palmitic acid, about 7.5%; stearic acid, about 2.5%; oleic acid, about 16.0%; and linoleic acid, about 1.0%.

24. A method for providing the agent of any one of claims 9 to 23 inclusive, characterized in that a liquid mixture of said fatty acids is fed to a spray nozzle, and that said fatty acid mixture is sprayed into a rising air stream carrying fine lime particles.

25. The method of claim 24 characterized in that the pressure gradient across said spray nozzle is from about 520 mm Hg to about 1560 mm Hg.

26. The method of claim 24 or claim 25 characterized in that the air flow velocity is within the range of about 910 M/min. to about 1820 M/min.

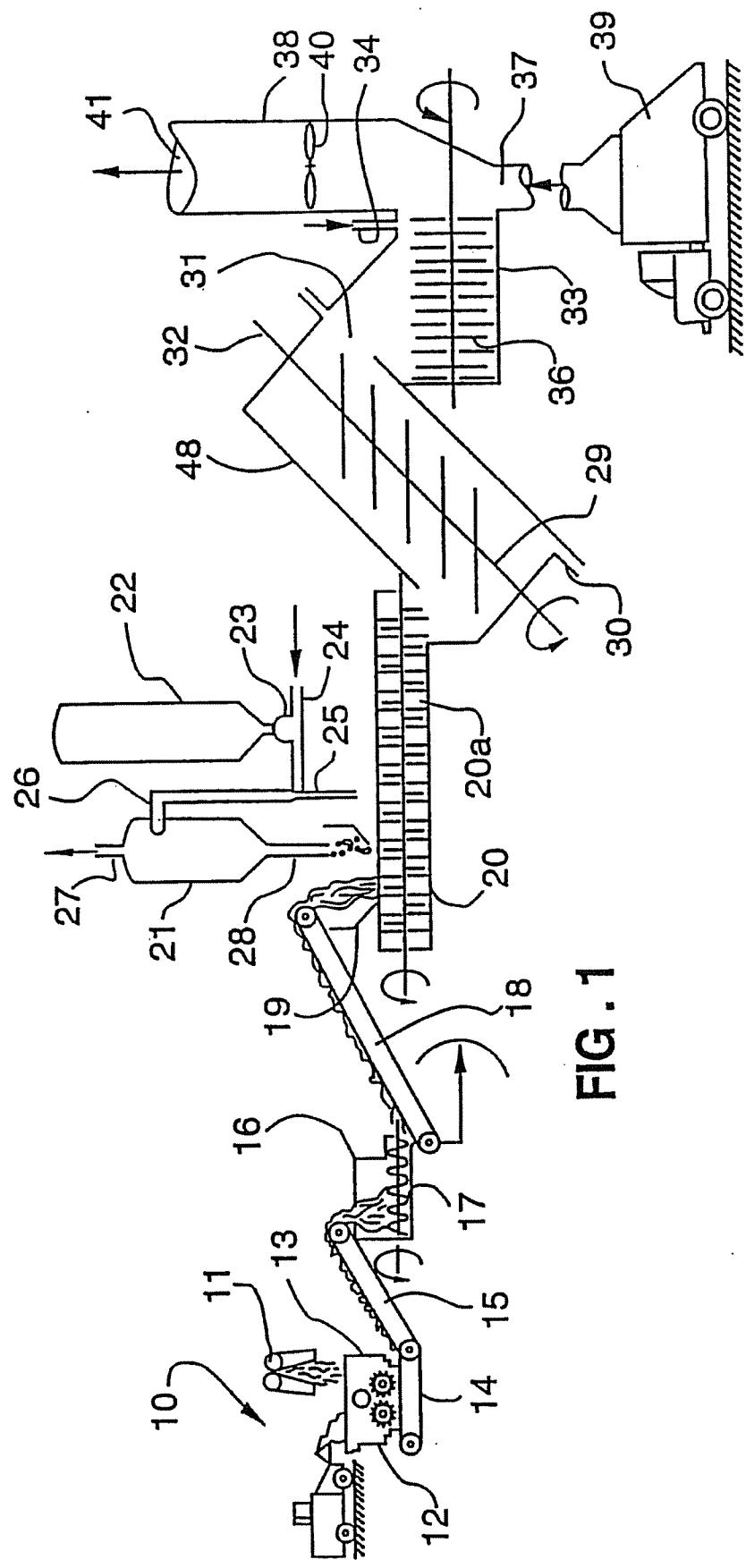


FIG. 1

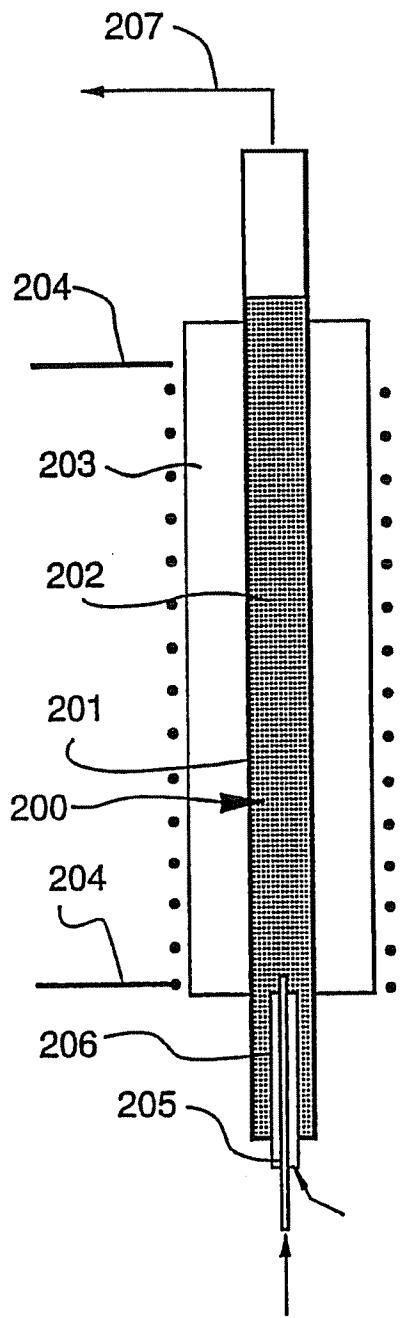


FIG .2

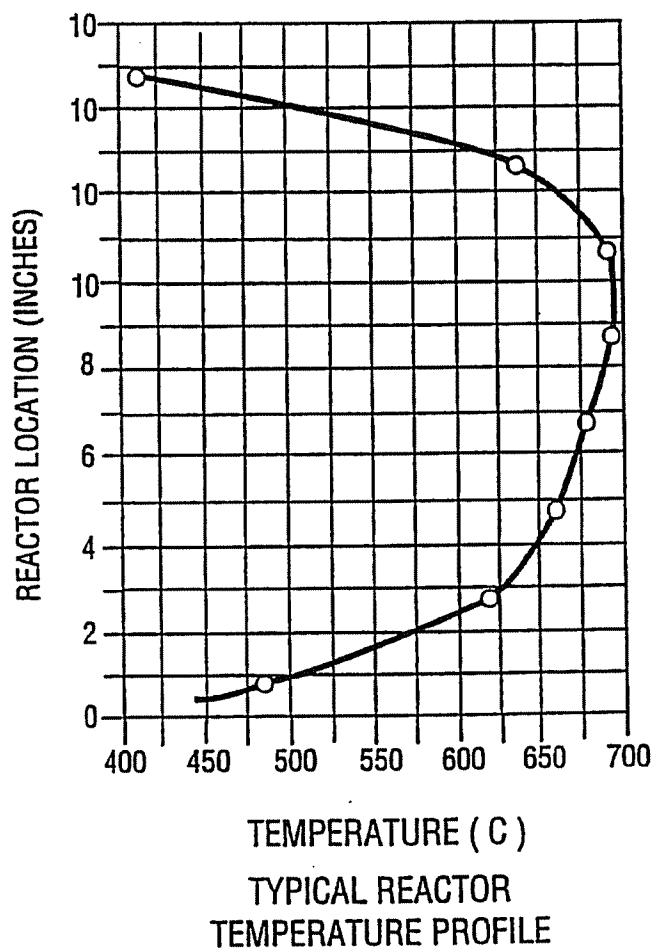
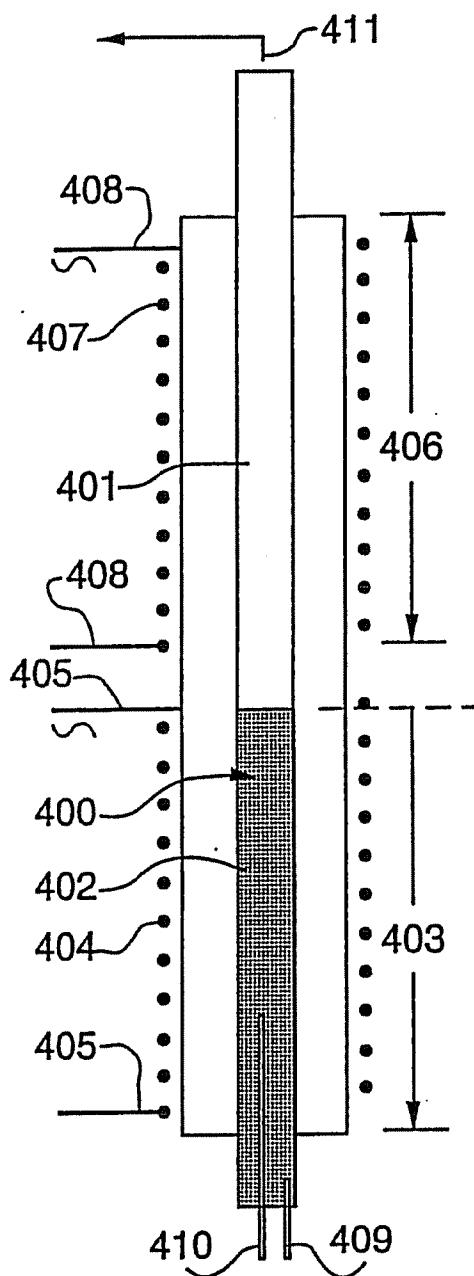
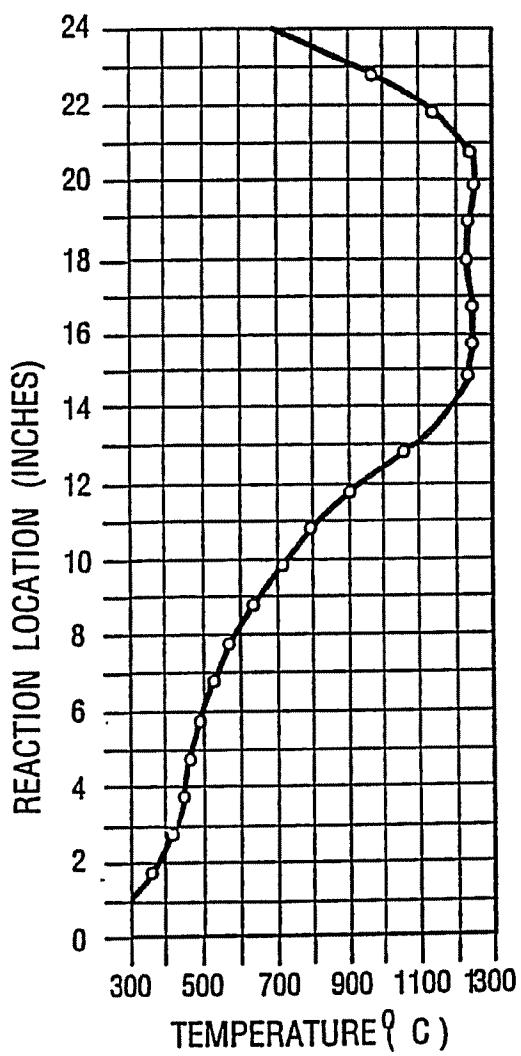


FIG .3

**FIG .4****TYPICAL FURNACE
TEMPERATURE PROFILE****FIG .5**



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 95 25 0091

DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int.Cl.6)	
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim		
X	EP-A-0 546 649 (R. RITTER)	10-26	B09C1/08	
A	* column 3, line 40 - column 5, line 52 * * column 11, line 16 - column 12, line 8 * * figure *	1-9	C09K3/32 C09K17/40 C02F11/00 C02F11/06 C02F1/72 A62D3/00	
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X	PATENT ABSTRACTS OF JAPAN vol. 14 no. 522 (C-778) ,15 November 1990 & JP-A-02 215881 (TAGUCHI YOSHIO) 28 August 1990, * abstract *	10-13, 18-23		
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TECHNICAL FIELDS SEARCHED (Int.Cl.6)			B09C C09K C02F	
The present search report has been drawn up for all claims				
Place of search	Date of completion of the search	Examiner		
THE HAGUE	31 July 1995	Laval, J		
CATEGORY OF CITED DOCUMENTS				
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document				
T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application I : document cited for other reasons & : member of the same patent family, corresponding document				